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(54) Title: MODIFIED PIGMENT PRODUCTS AND BLACK MATRIXES COMPRISING SAME

(55) Abstract: The present invention describes modified pigment products comprising a pigment having attached at least one photopolymerizable group and at least one ionic or ionizable group. Dispersions, black matrixes, and resin compositions comprising these modified pigment products are also disclosed.

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TITLE

**MODIFIED PIGMENT PRODUCTS AND BLACK MATRIXES
COMPRISING SAME**

BACKGROUND OF THE INVENTION1. Field of the Invention.

[0001] The present invention relates to modified pigment products and dispersions, black matrixes, and resin compositions comprising these modified pigment products.

2. Description of the Related Art.

[0002] Black matrix is a generic name for materials used in color displays to improve the contrast of an image by separating individual color pixels. In liquid crystal displays (LCDs), the black matrix is a thin film having high light-shielding capability and is formed between the three color elements of a color filter. In LCD's using thin film transistors (TFT), the black matrix also prevents the formation of photo-induced currents due to reflected light in the TFT.

[0003] Conventionally the black matrix layer in liquid crystal displays is manufactured by vapor deposition of Cr/CrO. Although chromium based films have excellent light-shielding capabilities, the metal vapor deposition process is expensive. In addition, chromium use and disposal is subject to increasingly restrictive environmental regulations. Chromium films also have low resistivity, which restricts the electrical design of LCDs to a subset of the possible design configurations.

[0004] Black pigments such as carbon black have been used in polymer compositions to make resistive black matrixes. However, typical systems have not been able to provide the desired balance of overall properties. For example, while a black matrix containing a carbon black pigment could provide the required light-shielding capabilities (that is, an optical density (OD) of greater than 3 at 1 micron

thickness), typically the film would have only a modest resistivity. Alternatively, if a highly resistive film were produced, the OD was typically low.

[0005] Modified pigments having attached organic groups have also been disclosed for use in a black matrix for color filters. While these materials provide black matrixes and dispersions with good overall performance, there remains a need for black matrixes with improved properties, in particular, resistivity and optical density.

SUMMARY OF THE INVENTION

[0006] The present invention relates to a modified pigment product comprising a pigment having attached at least one polymeric group. In one embodiment, the polymeric group comprises at least one photopolymerizable group and at least one ionic or ionizable group. In another embodiment, the polymeric group has the formula $-X-Sp-[PP]$, wherein X, which is directly attached to the pigment, represents an arylene, a heteroarylene, or an alkylene group and Sp represents a spacer group. The group PP represents a polymer comprising at least one photopolymerizable group and at least one acidic group. The modified pigments may also be in a liquid vehicle to form a dispersion.

[0007] The present invention further relates to a modified pigment product comprising a pigment having attached at least one polymeric group, wherein the pigment is carbon black having a dibutylphthalate adsorption (DBP) of about 25 to 70 mL/100g. The modified pigment may also be in a liquid vehicle to form a dispersion.

[0008] The present invention further relates to a black matrix formed by applying a photosensitive layer onto a substrate, irradiating the photosensitive layer imagewise, and developing and drying the coating. The photosensitive layer comprises a modified black pigment product as described above.

[0009] The present invention further relates to a resin composition comprising: a) a photosensitive resin and b) a modified pigment product as described above.

[0010] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention, as claimed.

DETAILED DESCRIPTION OF THE INVENTION

[0011] The present invention relates to modified pigment products, and black matrixes, dispersions, and resin compositions comprising the modified pigment products.

[0012] The modified pigment product of the present invention comprises a pigment having attached at least one polymeric group. The pigment can be any type of pigment, such as a black pigment and other colored pigments. Preferably the pigment is a carbon product, such as carbon black. Mixtures of different pigments can also be used. These pigments can also be used in combination with a variety of different types of dispersants in order to form stable dispersions.

[0013] Representative examples of black pigments include various carbon blacks (Pigment Black 7) such as channel blacks, furnace blacks and lamp blacks, and include, for example, carbon blacks sold under the Regal®, Black Pearls®, Elftex®, Monarch®, Mogul®, and Vulcan® trademarks available from Cabot Corporation (such as Black Pearls® 2000, Black Pearls® 1400, Black Pearls® 1300, Black Pearls® 1100, Black Pearls® 1000, Black Pearls® 900, Black Pearls® 880, Black Pearls® 800, Black Pearls® 700, Black Pearls® L, Elftex® 8, Monarch® 1400, Monarch® 1300, Monarch® 1100, Monarch® 1000, Monarch® 900, Monarch® 880, Monarch® 800, Monarch® 700, Mogul® L, Regal® 330, Regal® 400, Vulcan® P). Other suitable carbon blacks include, but are not limited to, Printex 40, Printex 80, Printex 300, Printex L, Printex U, Printex V, Special Black 4, Special Black 5, Special Black 250, FW200, (the foregoing available from Degussa Corporation), Raven 780, Raven 890, Raven 1020, Raven 1040, Raven 1255, Raven 1500, Raven 5000, Raven 5250 (the foregoing available from Colombian Chemical Corporation) and MA100 and MA440 available from Mitsubishi Chemical Corporation.

[0014] The pigment may also be chosen from a wide range of conventional colored pigments. The colored pigment can be blue, black, brown, cyan, green, white,

violet, magenta, red, orange, yellow, as well as mixtures thereof. Suitable classes of colored pigments include, for example, anthraquinones, phthalocyanine blues, phthalocyanine greens, diazos, monoazos, pyranthrone, perylenes, heterocyclic yellows, quinacridones, and (thio)indigoids. Representative examples of phthalocyanine blues include copper phthalocyanine blue and derivatives thereof (Pigment Blue 15). Representative examples of quinacridones include Pigment Orange 48, Pigment Orange 49, Pigment Red 122, Pigment Red 192, Pigment Red 202, Pigment Red 206, Pigment Red 207, Pigment Red 209, Pigment Violet 19 and Pigment Violet 42. Representative examples of anthraquinones include Pigment Red 43, Pigment Red 194 (Perinone Red), Pigment Red 216 (Brominated Pyranthrone Red) and Pigment Red 226 (Pyranthrone Red). Representative examples of perylenes include Pigment Red 123 (Vermillion), Pigment Red 149 (Scarlet), Pigment Red 179 (Maroon), Pigment Red 190 (Red), Pigment Violet 19, Pigment Red 189 (Yellow Shade Red) and Pigment Red 224. Representative examples of thioindigoids include Pigment Red 86, Pigment Red 87, Pigment Red 88, Pigment Red 181, Pigment Red 198, Pigment Violet 36, and Pigment Violet 38. Representative examples of heterocyclic yellows include Pigment Yellow 1, Pigment Yellow 3, Pigment Yellow 12, Pigment Yellow 13, Pigment Yellow 14, Pigment Yellow 17, Pigment Yellow 65, Pigment Yellow 73, Pigment Yellow 74, Pigment Yellow 151, Pigment Yellow 117, Pigment Yellow 128 and Pigment Yellow 138. Such pigments are commercially available in either powder or press cake form from a number of sources including, BASF Corporation, Engelhard Corporation and Sun Chemical Corporation. Examples of other suitable colored pigments are described in the Colour Index, 3rd edition (The Society of Dyers and Colourists, 1982).

[0015] Other examples of pigments include Hostafine® series such as Hostafine® Yellow GR (Pigment 13), Hostafine® Yellow (Pigment 83), Hostafine® Red FRL (Pigment Red 9), Hostafine® Rubine F6B (Pigment 184), Hostafine® Blue 2G (Pigment Blue 15:3), Hostafine® Black T (Pigment Black 7), and Hostafine® Black TS (Pigment Black 7), Normandy Magenta RD-2400, Paliogen Violet 5100, Paliogen® Violet 5890, Permanent Violet VT2645, Heliogen Green L8730, Argyle Green XP-111-S, Brilliant Green Toner GR 0991, Heliogen® Blue L6900, L7020, Heliogen® Blue D6840, D7080, Sudan Blue OS, PV Fast Blue

B2GO1, Irgalite Blue BCA, Paliogen® Blue 6470, Sudan III, Sudan II, Sudan IV, Sudan Orange G, Sudan Orange 220, Paliogen® Orange 3040, Ortho Orange OR 2673, Paliogen® Yellow 152, 1560, Lithol Fast Yellow 0991K, Paliotol Yellow 1840, Novoperm® Yellow FG 1, Permanent Yellow YE 0305, Lumogen Yellow D0790, Suco-Gelb L1250, Suco-Yellow D1355, Hostaperm® Pink E, Fanal Pink D4830, Cinquasia Magenta, Lithol Scarlet D3700, Toluidine Red, Scarlet for Thermoplast NSD PS PA, E.D. Toluidine Red, Lithol Rubine Toner, Lithol Scarlet 4440, Bon Red C, Royal Brilliant Red RD-8192, Oracet Pink RF, Paliogen® Red 3871K, Paliogen® Red 3340, and Lithol Fast Scarlet L4300. These are available from sources such as Hoechst Celanese Corporation, Paul Uhlich, BASF, American Hoechst, Ciba-Geigy, Aldrich, DuPont, Ugine Kuhlman of Canada, Dominion Color Company, Magruder, and Matheson, Coleman, Bell.

[0016] The pigment can have a wide range of BET surface areas, as measured by nitrogen adsorption. Preferably, the pigment has a surface area of from about 10 to 600 m²/g. More preferably, the surface area is from about 20 to 250 m²/g, and most preferably from about 20 to 100 m²/g. If the preferred surface area of the pigment is not readily available, it is well recognized by those skilled in the art that the pigment may be subject to conventional size comminution or reduction techniques, such as ball or jet milling, to reduce the pigment to the desired particle size.

[0017] The pigment can also have a wide range of dibutylphthalate absorption (DBP) values, which is a measure of the structure or branching of the pigment. Preferably the DBP value of the pigment is from about 25 to 70 mL/100g, more preferably from about 30 to 50 mL/100g, and most preferably from about 30 to 40 mL/100g. In addition, the pigment may have a wide range of primary particle sizes. It is preferred that the primary particle size is from about 10 to 100 nm, more preferably 15 to 60 nm. The preferred pigments approach an essentially overall spherical geometry. Pigments with other shapes, such as needles and plates, may also be used.

[0018] The modified pigment product of the present invention comprises a pigment having attached at least one polymeric group. The polymeric group can be any type of polymeric group capable of being attached to the pigment, such as, for example, a thermoplastic polymeric group or a thermosetting polymeric group. The polymeric group can be a random polymer, alternating polymer, graft polymer, block

polymer, star-like polymer, and/or comb-like polymer. In addition, the polymeric group can be a homopolymer, copolymer, terpolymer, and/or a polymer containing any number of different repeating units. Examples of polymeric groups include, but are not limited to, polycarbonates, polyethers, polyesters, polyacrylates, polymethacrylates, polystyrenes, polyamines, and polyolefins. Preferably, the polymeric group comprises a phenylether or bisphenyl ether and a substituted propanediyl group. For example, the polymeric group may be a polymer prepared from epoxy bisphenol-A, oligomers of epoxy bisphenol-A, or epoxy novolac. Another preferred polymeric group comprises styrene and maleic anhydride, maleic acid, or salts or derivatives thereof. For example, the polymeric group may be a polymer of styrene and a maleic anhydride half ester. Also, the polymeric group can be attached to the pigment at multiple points along the polymer chain through proper choice of substituent groups on the repeating monomer units.

[0019] In one embodiment of the present invention, the modified pigment product comprises a pigment having attached at least one polymeric group, wherein the polymeric group comprises at least one photopolymerizable group and at least one ionic or ionizable group. As used herein, the term "photopolymerizable group" is defined as any organic functional group capable of forming polymeric materials upon exposure to radiation, such as ultraviolet, infrared, or electron beam radiation. This includes groups which are photoreactive (that is, they form reactive species such as radicals upon exposure to radiation), also sometimes referred to as photoinitiators, as well as groups which react with the reactive species formed from photoreactive groups. Examples include azo groups and ethylenically unsaturated groups. Preferred photopolymerizable groups comprise acrylate groups, methacrylate groups, vinyl groups, and styrenic groups. Most preferred are acrylate esters and methacrylate esters.

[0020] For this embodiment, the polymeric group further comprises at least one ionic or ionizable group. As used herein, an "ionic group" is either anionic or cationic and is associated with a counterion of the opposite charge, and an "ionizable group" is one that is capable of forming an ionic group in the medium of use.

[0021] The polymeric group may comprise at least one anionic or anionizable group. Anionic groups are negatively charged ionic groups that may be generated

from groups having ionizable substituents that can form anions (anionizable groups), such as acidic substituents. They may also be the anion in the salts of ionizable substituents. Preferably, when the ionizable substituent forms an anion, the ionizable substituent has a pK_a of less than 11. The anionic group could further be generated from a species having ionizable groups with a pK_a of less than 11 and salts of ionizable substituents having a pK_a of less than 11. The pK_a of the ionizable substituent refers to the pK_a of the ionizable substituent as a whole, not just the acidic substituent. More preferably, the pK_a is less than 10 and most preferably less than 9.

[0022] Representative examples of anionic groups include $-COO^-$, $-SO_3^-$, $-OSO_3^-$, $-HPO_3^-$, $-PO_3^{2-}$, $-OPO_3^{2-}$, $-RS^-$, $-R'O^-$, and representative examples of anionizable groups include $-COOH$, $-SO_3H$, $-PO_3H_2$, $-R'SH$, $-R'OH$, and $-SO_2NHCOR'$, wherein R' represents a substituted or unsubstituted aryl and/or alkyl group. Preferably, the anionic or anionizable group comprises a carboxylic acid group, a sulfonic acid group, a phosphonic acid group, or salts thereof. Most preferred is a carboxylic acid group or salt thereof.

[0023] The polymeric group may comprise at least one cationic or cationizable group. Cationic groups are positively charged organic ionic groups that may be generated from ionizable substituents that can form cations (cationizable groups), such as amines. For example, alkyl or aryl amines may be protonated in acidic media to form ammonium groups $-NR'_2H^+$, where R' represent an organic group such as a substituted or unsubstituted aryl and/or alkyl group. Preferably, the amine has a pK_b of less than 5. Cationic groups may also be positively charged organic ionic groups. Examples include quaternary ammonium groups ($-NR'_3^+$) and quaternary phosphonium groups ($-PR'_3^+$). Here, R' represents hydrogen or an organic group such as a substituted or unsubstituted aryl and/or alkyl group. Preferably, the cationic or cationizable group comprises an amine group or a salt thereof.

[0024] In a second embodiment of the present invention, the modified pigment product comprises a pigment having attached at least one polymeric group, wherein the polymeric group has the formula $-X-Sp-[PP]$. X, which is directly attached to the pigment, represents an arylene or heteroarylene group or an alkylene group and is substituted with an Sp group. Sp represents a spacer group. The group PP represents

a polymeric group comprising repeating monomer groups or multiple monomer groups or both. The polymeric group optionally comprises at least one photopolymerizable group, optionally at least one ionic or ionizable group, or optionally both. Preferably the polymeric group comprises at least one photopolymerizable group. More preferably, the polymeric group further comprises at least one ionic or ionizable group. The polymeric group can also be further substituted with additional groups. The total number of monomer repeating units that comprise the group PP is preferably not greater than about 500 monomer repeating units, and more preferably is not greater than about 100 monomer repeating units.

[0025] The group PP can be any type of polymeric group, as described above, such as, for example, a homopolymer, copolymer, terpolymer, and/or a polymer containing any number of different repeating units. Further, the group PP can be a random polymer, alternating polymer, graft polymer, block polymer, star-like polymer, and/or comb-like polymer. Preferred examples of the group PP are those described above.

[0026] The group Sp represents a spacer group which, as used herein, is a link between two groups. The group Sp can be a bond or a chemical group. Examples of chemical groups include, but are not limited to, $-\text{CO}_2-$, $-\text{O}_2\text{C}-$, $-\text{CO}-$, $-\text{OSO}_2-$, $-\text{SO}_3-$, $-\text{SO}_2-$, $-\text{SO}_2\text{C}_2\text{H}_4\text{O}-$, $-\text{SO}_2\text{C}_2\text{H}_4\text{S}-$, $-\text{SO}_2\text{C}_2\text{H}_4\text{NR}-$, $-\text{O}-$, $-\text{S}-$, $-\text{NR}-$, $-\text{NRCO}-$, $-\text{CONR}-$, $-\text{NRCO}_2-$, $-\text{O}_2\text{CNR}-$, $-\text{NRCONR}-$, $-\text{NRCOCH}(\text{CH}_2\text{CO}_2\text{R})-$, $-\text{NRCOCH}_2\text{CH}(\text{CO}_2\text{R})-$, $-\text{N}(\text{COR})(\text{CO})-$, $-\text{OOC-Alk-COO}-$, $-\text{OOC-Alk-CONR}-$, $-\text{OOC-Alk-CONR}(\text{CH}_2\text{-CH}_2)_x\text{NR}-(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, $-\text{OOC-Alk-COO}(\text{CH}_2\text{-CH}_2)_x\text{O}-(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, $-\text{OOC-Alk-COO(AOX)}_x\text{-(CH}_2\text{-CH}_2)\text{-SO}_2-$, $-\text{OOC-Alk-CONR(AOX)}_x\text{-Alk-NR-(CH}_2\text{-CH}_2)\text{-SO}_2-$, $-\text{O-(CH}_2\text{-CH}_2)\text{-SO}_2-$, imide groups, arylene groups, alkylene groups and the like. R, which can be the same or different, represents hydrogen or an organic group such as a substituted or unsubstituted aryl or alkyl group, Alk represents a saturated or unsaturated cyclic or linear alkylene group such as a cyclohexanediyl group, AOX represents an alkylene oxide group of from about 1 to about 12 carbons, and x is an integer between 1 and 500,

[0027] The group X represents an arylene or heteroarylene group or an alkylene group. X is directly attached to the pigment and is further substituted with an

Sp group. The aromatic group can be further substituted with any group, such as one or more alkyl groups or aryl groups. Preferably, the arylene group is phenylene, naphthylene, or biphenylene, and the heteroarylene group. When X represents an alkylene group, examples include, but are not limited to, substituted or unsubstituted alkylene groups which may be branched or unbranched. The alkylene group can be substituted with one or more groups, such as aromatic groups. Examples include, but are not limited to, C₁-C₁₂ groups like methylene, ethylene, propylene, or butylene, groups. Preferably, X is an arylene group.

[0028] The group X may be substituted with one or more functional groups. Examples of functional groups include, but are not limited to, R", OR", COR", COOR", OCOR", carboxylates, halogens, CN, NR"₂, SO₃H, sulfonates, sulfates, NR"(COR"), CONR"₂, NO₂, PO₃H₂, phosphonates, phosphates, N=NR", SOR", NSO₂R", wherein R" which can be the same or different, is independently hydrogen, branched or unbranched C₁-C₂₀ substituted or unsubstituted, saturated or unsaturated hydrocarbons, e.g., alkyl, alkenyl, alkynyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, substituted or unsubstituted alkaryl, or substituted or unsubstituted aralkyl.

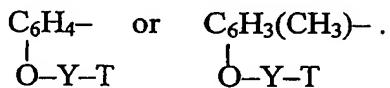
[0029] As shown by the structure above, the group PP is attached to the pigment through the spacer group Sp. In addition, the group PP can also be attached to the pigment at multiple points along the polymer chain through proper choice of substituent groups on the repeating monomer units. These substituents may also comprise spacer groups or -X-Sp- groups as described above. Thus, these groups can be attached to the pigment at either end or at points along the backbone. Further, these groups can be any type of polymeric group, such as a random polymer, alternating polymer, graft polymer, block polymer, star-like polymer, and/or comb-like polymer.

[0030] In one preferred embodiment, the group PP represents a polymer having the formula [T-Y-(Q-Y)_n-T], wherein n represent the number of repeating units Q-Y in the polymer and is an integer from 1 to 20. Q comprises a bisphenyl ether group such as, for example, -O-C₆H₄-C(CH₃)₂-C₆H₄-O-, -O-C₆H₄-CH₂-C₆H₄-O-, or -O-C₆H₄-fluorenyl-C₆H₄-O-. Y comprises a substituted propanediyl group and

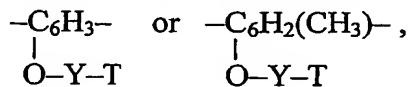
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includes groups having the formula $-\text{CH}_2-\text{CH}(\text{Z})-\text{CH}_2-$, wherein Z is $-\text{OH}$ or $-\text{OOC-Alk-COOH}$, or salt thereof. Alk represents a saturated or unsaturated cyclic or linear alkyl group, such as a cyclohexanediyl group. Z may also be a bond to the spacer group, Sp. In this case, preferred space groups Sp include $-\text{OOC-Alk-COO}-$, $-\text{OOC-Alk-CONR}-$, $-\text{OOC-Alk-CONR}(\text{CH}_2-\text{CH}_2)_x\text{NR}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, $-\text{OOC-Alk-COO}(\text{CH}_2-\text{CH}_2)_x\text{O}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, $-\text{OOC-Alk-COO}(\text{AOX})_x-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, $-\text{OOC-Alk-CONR}(\text{AOX})_x\text{-Alk-NR}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, or $-\text{O}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, wherein R, which can be the same or different, is hydrogen or a substituted or unsubstituted aryl or alkyl group, AOX represents an alkylene oxide group of from about 1 to about 12 carbons, and x is an integer between 1 and 500. T represents a terminating group and includes, for example, alkyl ester groups such as acetate and propionate. Preferably, T further comprises the photopolymerizable group and may be a group such as $\text{CH}_2=\text{CH-COO-}$ or $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COO-}$.

[0031] In a second preferred embodiment, the group PP represents a polymer having the formula $[\text{A}-(\text{CR}_2\text{B})_n-\text{CR}_2\text{A}]$, wherein n represent the number of repeating units B in the polymer and is an integer from 1 to 20. R, which can be the same or different, is hydrogen or a substituted or unsubstituted aryl or alkyl group. A and B comprise a phenyl ether group and a substituted propanediyl group, and may further comprise the photopolymerizable group. Examples of group A include groups having the formula:



Examples of group B include groups having the formula:



Y and T are as described above.

[0032] The modified pigments of the present invention are modified using methods known to those skilled in the art such that organic groups are attached to the pigment. For example, the modified pigments used in the dispersions of the present invention can be prepared using the methods described in U.S. Patent Nos. 5,851,280, 5,698,016, 5,922,118, and 5,837,045, and PCT Publication Nos. WO 99/51690 and WO 00/22051, the descriptions of which are fully incorporated herein by reference.

This provides a more stable attachment of the groups on the pigment compared to adsorbed groups, such as polymers, surfactants, and the like.

[0033] The modified pigments may also comprise a pigment having attached at least one organic group, wherein the organic group comprises the reaction product of a pigment having attached a first chemical group with a second chemical group to form a pigment having attached a third organic group. For this, the modified pigments can be prepared using methods known to those skilled in the art. For example, the modified pigments may be prepared using the method described in PCT Publication No. WO 01/51566, which is incorporated in its entirety herein by reference. Thus, for example, the organic group may comprise the reaction product of at least one electrophile, such as a (2-sulfatoethyl)-sulphone group or a benzoic acid group, and at least one nucleophilic polymer, such as a polyamine or an amine derivative of an epoxy bisphenol-A polymer. Further reactions on these attached organic groups, such as acylation reactions, are also possible. Other examples are also disclosed in the above cited reference.

[0034] The amount of the attached polymeric groups can be varied in order to attain the desired performance attributes. Preferably, the total amount of attached polymeric groups is from about 0.001 to about 10.0 micromoles of polymeric group/m² surface area of pigment, as measured by nitrogen adsorption (BET method). More preferably, the amount of attached polymeric groups is between from about 0.01 to about 5.0 micromoles/m² and most preferably is between from about 0.05 to 3.0 micromoles/m². In addition, the modified pigments may further comprise additional attached organic groups. This can result in further improved properties. In one preferred embodiment, the modified pigment comprises a polymeric group and an ionic group, ionizable group, or mixture of ionic and ionizable groups. Examples include those described above for attached polymeric groups comprising ionic or ionizable groups. Preferably the ionic or ionizable group comprises a carboxylic acid, a sulfonic acid group, or salts thereof.

[0035] The modified pigments may be purified by washing, such as by filtration, centrifugation, or a combination of the two methods, to remove unreacted raw materials, byproduct salts and other reaction impurities. The products may also

be isolated, for example, by evaporation or it may be recovered by filtration and drying using known techniques to those skilled in the art.

[0036] The modified pigment products of the present invention can be also be combined with a liquid vehicle to form a dispersion. The type of liquid will depend on the type and amount of polymeric groups attached to the modified pigment. While both aqueous and non-aqueous liquid vehicles can be used, preferably the liquid vehicle is a non-aqueous vehicle. Examples include non-aqueous vehicles comprising ethylcellosolve, ethylcellosolve acetate, butylcellosolve, butylcellosolve acetate, ethylcarbitol, ethylcarbitol acetate, diethyleneglycol, cyclohexanone, propyleneglycol monomethylether, propyleneglycol monomethylether acetate, lactate esters, and mixtures thereof. Aqueous solvents may also be added, including, for example, water and water soluble alcohols.

[0037] The modified pigment products may be formed into a dispersion using any method known to those skilled in the art, including, for example, using high shear mixing. The amount of modified pigment can be between about 1% and 60% based on the total weight of dispersion, and is preferably between about 5% to 30% by weight. The dispersions can be formed with a minimum of additional components (additives and/or cosolvents) and processing steps. However, additives such as surfactants and cosolvents may also be included. For example, a photosensitive resin, such as epoxy bisphenol-A or epoxy novolak, can be added.

[0038] The modified pigments formed into a dispersion may also be further purified or classified to remove impurities and other undesirable free species which can co-exist in the dispersion as a result of the manufacturing process. For example, the dispersion can be purified to remove any undesired free species, such as unreacted treating agent. Known techniques of ultrafiltration/diafiltration using a membrane or ion exchange may be used to purify the dispersion and remove a substantial amount of free ionic and unwanted species. An optional exchange of counterions step may also occur in the purification process whereby the counterions that may form a part of the modified pigment are exchanged or substituted with alternative counterions (including, e.g., amphiphilic ions) utilizing known ion exchange techniques such as ultrafiltration, reverse osmosis, ion exchange columns and the like. Particular

examples of counterions that can be exchanged include, but are not limited to, Na^+ , K^+ , Li^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Cl^- , NO_3^- , NO_2^- , acetate, and Br^- .

[0039] The present invention further relates to a black matrix. As described above, a black matrix is formed by applying a photosensitive layer onto a substrate, irradiating the photosensitive layer imagewise, and developing and drying the coating. For the black matrixes of the present invention, the photosensitive layer comprises a modified black pigment product comprising a black pigment having attached at least one polymeric group. Preferably, the black pigment is a carbon product, and most preferably is carbon black. The carbon black can have a wide range of surface area, structure, and primary particle size, as described above, but preferably has a DBP value of from about 25 to 70 mL/100g.

[0040] The polymeric group may be any of the polymeric groups described above. Thus, the polymeric group can comprise at least one photopolymerizable group and at least one ionic or ionizable group. For example, the polymeric group may be a group represented by the formula $-\text{X}-\text{Sp}-[\text{PP}]$, where X, Sp, and PP are as defined above.

[0041] The choice of ionic or ionizable group will depend on the method used for developing the black matrix. For example, if an alkaline developer is used, the ionic or ionizable group will preferably be an anionic or anionizable group. If an acidic developer is used, a cationic or cationizable group is preferred.

[0042] The black matrix of the present invention may further comprise a photosensitive resin, such as, for example, resins prepared from an epoxy bisphenol-A or an epoxy novolac. Other photosensitive resins will be known to those skilled in the art.

[0043] The volume resistivity and optical density are important properties for a black matrix material. Volume resistivity is a measure of the ability of a material to prevent the conduction of electricity and can be measured using techniques known in the art, for example, as defined in ASTM procedure D257-93. Optical density (OD) is a measure of the opacity of a material and is typically measured using a densitometer. OD is dependent on several factors, including the thickness of the film. The black matrixes of the present invention preferably have a volume resistivity of greater than

or equal to 10^{13} ohm-cm. More preferably, the black matrixes of the present invention also have an optical density of greater than about 3 at a film thickness of 1 micron.

[0044] The amount of the attached polymeric groups of the modified pigments in the black matrixes of the present invention can be varied in order to attain the desired overall performance attributes. The total amount of attached polymeric groups is as described above and can range from about 0.001 to about 10.0 micromoles of polymeric group/m² surface area of pigment, as measured by nitrogen adsorption (BET method), more preferably from about 0.01 to 5.0 micromoles/m², and most preferably from about 0.05 to 3.0 micromoles/m².

[0045] The photosensitive layer of the black matrixes of the present invention comprise an amount of modified black pigment product effective to attain the desired overall properties. The amount of modified black pigment will depend on the type of pigment and the amount of attached polymeric groups. Preferably, the amount of modified black pigment in the photosensitive layer is between 10% and 70%, more preferably 20% to 60%, and most preferably, 30% to 50%. It has been found that a lower level of these modified black pigments are needed to produce the desired overall properties compared to conventional black pigments.

[0046] While not wishing to be bound by theory, it is believed that the attached polymeric groups of the modified pigment products of the present invention separate the pigment particles and thereby reduce the conductivity of a black matrix that incorporates the pigment particles. In addition, it is believed that the modified pigments comprising a pigment having attached at least one polymeric group having the formula -X-Sp-[PP] have a uniform distribution of attached groups. This leads to a more effective separation of particles and results in a very high volume resistivity in a black matrix. It is believed that, in general, higher densities of attached groups lead to higher volume resistivities. The attached polymeric groups also allow the modified pigments to be dispersed well within the photosensitive layer, thereby resulting in high OD, even at relatively low loadings. The presence of a photopolymerizable group enables the modified pigment to react upon irradiation, thus becoming crosslinked within the photosensitive layer. The ionic or ionizable group enables any non-photopolymerized material to be developable.

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[0047] The present invention further relates to a resin composition comprising: a) a photosensitive resin and b) a modified pigment product, wherein the resin composition has been cured by irradiation. The resin composition may further comprise a photoinitiator. The modified pigment product is as described above and comprises a pigment having attached at least one polymeric group, wherein the polymeric group comprises at least one photopolymerizable group and at least one ionic or ionizable group. For example, the polymeric group may have the formula —X-Sp-[PP], wherein X, Sp, and PP are as described above. Preferably the pigment is carbon black having a dibutylphthalate adsorption (DBP) of from about 25 to 70 mL/100g. The photosensitive resin can be any of those known to one skilled in the art, such as, for example, an epoxy bisphenol-A resin or an epoxy novolac resin. The resin composition may be cured by any source of radiation such as, for example, infrared or ultraviolet radiation.

[0048] The present invention will be further clarified by the following examples which are intended to be only exemplary in nature.

EXAMPLES

Example 1 – Polymer Preparation

[0049] Acrylic acid (4.8 g) was slowly added at 66°C to a stirred solution of 30 g of bisphenol-A epoxy resin (EPON 1001F, available from Resolution Performance Products) in 30 g of THF. Tetraethyl ammonium bromide (0.2 g) was added as a catalyst and methoxyhydroquinone (0.1 g) as an antioxidant. The reaction was monitored by acid number measurements. After 30 hours of reaction in refluxing THF, hexahydrophthalic anhydride (10.5 g) was added to the reaction mixture and stirred for an additional 2 hr at the same temperature. The resulting carboxy acrylated polymer solution in THF was allowed to cool to room temperature and used without further isolation.

Example 2 – Modification of the Polymer

[0050] 1,4-phenylene diamine (2.95 g) was added to the polymer solution of Example 1 along with 250 mL of THF, and after dissolution, 5.6 g of

dicyclohexylcarbodiimide (DCC) was added. The reaction mixture was stirred for 2 hr at room temperature and purified by filtration to remove the precipitated urea.

Example 3 - Preparation of a Modified Pigment Product

[0051] Modified polymer solution of Example 2 and 30 g of carbon black were mixed in a rotor stator. The carbon black had a surface area of 50 m²/g and DBP of 46 mL/100g. Methanesulfonic acid (0.96 g) was added. A solution of 0.69 g of NaNO₂ in 10 g of water was added drop-wise, and mixing was continued for an additional 3 hr. The resulting dispersion was purified by diafiltration using first acetone/THF (20/80) solution followed by acetone and finally propylene glycol methoxy ether acetate (PGMEA). The resulting dispersion was filtered sequentially through a series of filters (20 micron, 5 micron, 1 micron, and 0.5 micron).

Example 4 – Preparation of a Polymer Film

[0052] The modified carbon black dispersion of Example 3 could be mixed with a carboxylated epoxy cresol novolac polymer solution in butoxy ethyl acetate (65% solids, Actilane 340 manufactured by Akros Chemicals). The resulting formulation could then be coated onto a stainless steel panel with a 1.5 mil bird bar and drying for 45 min in an oven at 90°C. The resulting dried film (40% modified carbon black and 60% polymer) would be expected to have a thickness of about 7 microns. The volume resistivity of the film could be measured according ASTM procedure D257-93. The resulting dried film would be expected to have good overall properties.

Example 5 – Modification of the Polymer

[0053] Actilane 340 (31.2g, 65% solution in butoxy ethyl acetate, a carboxylated epoxy cresol novolac polymer manufactured by Akros Chemicals) was dissolved in 300 mL of dry THF. 1,4-phenylene diamine (PDA, 1.68g) was added to the polymer solution. After dissolution of PDA, dicyclohexylcarbodiimide (DCC, 3.22g) was added. The reaction mixture was stirred for 24 hours at room temperature under argon and purified by filtration to remove the precipitated urea.

Example 6 – Modification of the Polymer

[0054] Actilane 340 (150g, 65% solution in butoxy ethyl acetate, a carboxylated epoxy cresol novolac polymer manufactured by Akros Chemicals) was dissolved in 700 mL of dry N-methyl pyrrolidone (NMP). 1,4-phenylene diamine (PDA, 6.55g) was added to the polymer solution. After dissolution of PDA, dicyclohexylcarbodiimide (DCC, 60 mL of 1 M solution in methylene chloride) was added drop-wise. The reaction mixture was stirred for 19 hours at room temperature under argon and purified by filtration to remove the precipitated urea.

Example 7 – Modification of the Polymer

[0055] Sarbox SB404 (30g, 55% solution in PGMEA, a polymer of styrene and maleic acid half ester with hydroxyethyl acrylate manufactured by Sartomer) was dissolved in 150 mL of NMP. 1,4- phenylene diamine (PDA, 1.08g) was added to a polymer solution. After dissolution of PDA, dicyclohexylcarbodiimide (DCC, 2.78g) was added. The reaction mixture was stirred for 24 hours at room temperature under argon and purified by filtration to remove the precipitated urea.

Example 8 – Preparation of a Modified Pigment Product

[0056] Modified polymer solution of Example 5 and 30 g of carbon black were mixed in a rotor stator and brought to a temperature of 40°C. The carbon black had a surface area of 50 m²/g and DBP of 46 mL/100g. Methanesulfonic acid (0.95g) was added. A solution of 0.75g of NaNO₂ in 10 g of water was added drop-wise, and mixing was continued for an additional 3 hours at 40°C. The resulting dispersion was purified by diafiltration using first water/THF (10/90) mixture followed by THF and finally PGMEA. The resulting dispersion comprised a modified pigment product having a polymer attachment level of 26% as determined by TGA and had a solids content of 20.7%.

Example 9 – Preparation of a Modified Pigment Product

[0057] Carbon black (150g) with a surface area of 50 m²/g and DBP of 46 mL/100g, 1400 mL of NMP, and 100 mL of water were mixed in a rotor stator at 55°C. Sulfanilic acid (5.7g) was added and stirred for 10 min. NaNO₂ (4.5g) was dissolved

in 10 mL of water and slowly added. The reaction mixture was then mixed with a rotor stator for 2 hours.

[0058] Modified polymer solution from Example 6 was added to this reaction mixture in the rotor stator. Methanesulfonic acid (10.8g) was also added, and the temperature was increased to 55°C. Finally, a solution of 4.5 g of NaNO₂ in 10 g of water was slowly added. The reaction mixture was mixed with rotor stator for an additional 2 hours. The resulting dispersion was purified by diafiltration using first water/NMP (10/90) mixture followed by NMP and finally PGMEA. The resulting dispersion comprised a modified pigment product having a polymer attachment level of 34.8% as determined by TGA and had a solids content of 17.3%.

Example 10 – Preparation of a Modified Pigment Product

[0059] Modified polymer solution of Example 7 and 30 g of carbon black were mixed in a rotor stator and brought to a temperature of 55°C. The carbon black had a surface area of 50 m²/g and DBP of 46 mL/100g. Methanesulfonic acid (0.95g) was added. A solution of 0.75g of NaNO₂ in 10 g of water was added drop-wise, and mixing was continued for additional 3 hours at 55°C. The resulting dispersion was purified by diafiltration using first water/NMP (10/90) mixture followed by NMP and finally PGMEA. The resulting dispersion comprised a modified pigment product having a polymer attachment level of 29.8% as determined by TGA and had a solids content of 18.5%.

Example 11 – Preparation of a Modified Pigment Product

[0060] Carbon black (150g) with a surface area of 100 m²/g and DBP of 31 mL/100g, 1400 mL of NMP, and 100 mL of water were mixed in a rotor stator at 55°C. Sulfanilic acid (5.7g) was added and stirred for 10 min. NaNO₂ (4.5g) was dissolved in 10 mL of water and slowly added. The reaction mixture was then mixed with a rotor stator for 2 hours.

[0061] Modified polymer solution from Example 6 was added to this reaction mixture in the rotor stator. Methanesulfonic acid (10.8g) was also added, and the temperature was increased to 55°C. Finally, a solution of 4.5 g of NaNO₂ in 10 g of water was slowly added. The reaction mixture was mixed with rotor stator for an

additional 2 hours. The resulting dispersion was purified by diafiltration using first water/NMP (10/90) mixture followed by NMP and finally PGMEA. The resulting dispersion comprised a modified pigment product having a polymer attachment level of 17.6% as determined by TGA and had a solids content of 16.9%.

Example 12 – Preparation of a Polymer Film

[0062] The modified carbon black dispersions of Examples 8, 9, 10, and 11 were mixed with Actilane 340 (65% solids, manufactured by Akros Chemicals) and PGMEA to have an approximate solids content of 20%.

[0063] For volume resistivity measurements, the resulting formulations were coated onto a steel Q-panel with a 1 micron doctor's blade and dried for 45 min in an oven at 90°C. The resulting dried films (40% modified carbon black and 60% polymer, 45% modified carbon black and 55% polymer, and 50% modified carbon black and 50% polymer) had a thickness of about 5-8 microns (as measured on a KLA Tencor Alpha Step 500 Surface Profilometer). The volume resistivity of the films was measured using a Keithley Model 65 instrument equipped with an ETS 803B resistivity probe using alternating polarity methods. The applied voltage for most measurements was +/- 5V.

[0064] For optical density (OD) measurements, the formulations were spin coated on glass slides and dried for 45 min in an oven at 90°C. The resulting dried films (40% modified carbon black and 60% polymer, 45% modified carbon black and 55% polymer, and 50% modified carbon black and 50% polymer) had a thickness of about 0.6-1.7 microns (as measured on a KLA Tencor Alpha Step 500 Surface Profilometer). OD was measured using an X-Rite 361T Transmission Densitometer.

[0065] The resulting dried films from the dispersion of Example 8 had volume resistivities of 1.2×10^{14} ohm-cm (40% modified carbon black) and 2×10^{14} ohm-cm (50% modified carbon black). The dried films from the dispersion of Example 9 had volume resistivities of 6.5×10^{13} ohm-cm (40% modified carbon black), 5.4×10^{13} ohm-cm (45% modified carbon black) and 7×10^{13} ohm-cm (50% modified carbon black). The dried films from the dispersion of Example 10 had volume resistivities of 3.5×10^{13} ohm-cm (40% modified carbon black). The dried films from the dispersion of Example 11 had volume resistivities of 7×10^{13} ohm-cm (40% modified carbon

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black) and 3×10^{13} ohm-cm (45% modified carbon black). Optical densities were generally found to be about $3.0/\mu\text{m}$, particularly for films containing 50% modified carbon black. Therefore, a good combination of properties, in particular electrical and optical properties, were found for films prepared using the modified pigment products of the present invention.

[0066] The foregoing description of preferred embodiments of the present invention has been presented for the purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed. Modifications and variations are possible in light of the above teachings, or may be acquired from practice of the invention. The embodiments were chosen and described in order to explain the principles of the invention and its practical application to enable one skilled in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto, and their equivalents.

[0067] What is claimed is:

CLAIMS

1. A modified pigment product comprising a pigment having attached at least one polymeric group, wherein the polymeric group comprises at least one photopolymerizable group and at least one ionic or ionizable group.
2. The modified pigment product of claim 1, wherein the ionic or ionizable group is an anionic or anionizable group.
3. The modified pigment product of claim 1, wherein the pigment is carbon black.
4. The modified pigment product of claim 3, wherein the carbon black has a dibutylphthalate absorption (DBP) of from about 25 to 70 mL/100g.
5. The modified pigment product of claim 4, wherein the carbon black has a dibutylphthalate absorption (DBP) of from about 30 to 50 mL/100g.
6. The modified pigment product of claim 5, wherein the carbon black has a dibutylphthalate absorption (DBP) of from about 30 to 40 mL/100g.
7. The modified pigment product of claim 1, wherein the photopolymerizable group comprises an ethylenically unsaturated group.
8. The modified pigment product of claim 1, wherein the photopolymerizable group comprises an acrylate group, a methacrylate group, a vinyl group, or a styrenic group.
9. The modified pigment product of claim 8, wherein the photopolymerizable group is an acrylate ester or methacrylate ester.

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10. The modified pigment product of claim 2, wherein the anionic or anionizable group comprises a carboxylic acid or salt thereof.
11. The modified pigment product of claim 2, wherein the anionic or anionizable group is a group having the formula $-\text{OOC-Alk-COOH}$ or salt thereof, wherein Alk represents a saturated or unsaturated cyclic or linear alkyl group.
12. The modified pigment product of claim 11, wherein Alk represents a cyclohexanediyi group.
13. The modified pigment product of claim 1, wherein the polymeric group comprises a phenyl ether group and a substituted propanediyl group.
14. The modified pigment product of claim 1, wherein the polymeric group comprises a polymer prepared from epoxy bisphenol-A, oligomers of epoxy bisphenol-A, or epoxy novolac.
15. The modified pigment product of claim 1, wherein the modified pigment product is in a liquid vehicle to form a dispersion.
16. The modified pigment product of claim 15, wherein the liquid vehicle is a non-aqueous vehicle comprising a solvent selected from the group consisting of: ethylcellosolve, ethylcellosolve acetate, butylcellosolve, butylcellosolve acetate, ethylcarbitol, ethylcarbitol acetate, diethyleneglycol, cyclohexanone, propyleneglycol monomethylether, propyleneglycol monomethylether acetate, lactate esters, and mixtures thereof.
17. The modified pigment product of claim 15, further comprising a photosensitive resin.
18. The modified pigment product of claim 17, wherein the photosensitive resin is a resin prepared from an epoxy bisphenol-A resin or an epoxy novolac resin.

19. A modified pigment product comprising a pigment having attached at least one polymeric group having the formula $-X\text{-Sp-[PP]}$, wherein X, which is directly attached to the pigment, represents an arylene, a heteroarylene, or an alkylene group, Sp represents a spacer group, and PP represents a polymer comprising at least one photopolymerizable group and at least one ionic or ionizable group.
20. The modified pigment product of claim 19, wherein the ionic or ionizable group is an anionic or anionizable group.
21. The modified pigment product of claim 19, wherein the pigment is carbon black.
22. The modified pigment product of claim 21, wherein the carbon black has a dibutylphthalate absorption (DBP) of from about 25 to 70 mL/100g.
23. The modified pigment product of claim 22, wherein the carbon black has a dibutylphthalate absorption (DBP) of from about 30 to 50 mL/100g.
24. The modified pigment product of claim 23, wherein the carbon black has a dibutylphthalate absorption (DBP) of from about 30 to 40 mL/100g.
25. The modified pigment product of claim 19, wherein the photopolymerizable group comprises an ethylenically unsaturated group.
26. The modified pigment product of claim 19, wherein the photopolymerizable group comprises an acrylate group, a methacrylate group, a vinyl group, or a styrenic group.
27. The modified pigment product of claim 19, wherein the photopolymerizable group is an acrylate ester or methacrylate ester.

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28. The modified pigment product of claim 20, wherein the anionic or anionizable group comprises a carboxylic acid or salt thereof.
29. The modified pigment product of claim 20, wherein the anionic or anionizable group is a group having the formula $-\text{OOC-Alk-COOH}$ or salt thereof, wherein Alk represents a saturated or unsaturated cyclic or linear alkyl group.
30. The modified pigment product of claim 29, wherein Alk represents a cyclohexanediyl group.
31. The modified pigment product of claim 19, wherein the polymeric group comprises a phenyl ether group and a substituted propanediyl group.
32. The modified pigment product of claim 19, wherein the polymeric group comprises a polymer prepared from epoxy bisphenol-A, oligomers of epoxy bisphenol-A, or epoxy novolac.
33. The modified pigment product of claim 19, wherein PP represents a polymer having the formula $[\text{T-Y-(Q-Y)}_n\text{-T}]$, wherein Q comprises a bisphenyl ether group, Y comprises a substituted propanediyl group, T comprises a terminating group, and n is an integer from 1 to 20.
34. The modified pigment product of claim 33, wherein T comprises the photopolymerizable group.
35. The modified pigment product of claim 33, wherein T comprises an alkyl ester.
36. The modified pigment product of claim 33, wherein:
Q is $-\text{O-C}_6\text{H}_4\text{-C(CH}_3\text{)}_2\text{-C}_6\text{H}_4\text{-O-}$, $-\text{O-C}_6\text{H}_4\text{-CH}_2\text{-C}_6\text{H}_4\text{-O-}$, or $-\text{O-C}_6\text{H}_4\text{-fluorenyl-C}_6\text{H}_4\text{-O-}$;

Y is $-\text{CH}_2\text{-CH}(\text{Z})\text{-CH}_2-$, wherein Z is $-\text{OH}$, $-\text{OOC-Alk-COOH}$, or salt thereof, or a bond to Sp, and Alk represents a saturated or unsaturated cyclic or linear alkyl group; and

T is $\text{CH}_2=\text{CH-COO-}$ or $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COO-}$.

37. The modified pigment product of claim 36, wherein Sp is $-\text{OOC-Alk-COO-}$, $-\text{OOC-Alk-CONR-}$, $-\text{OOC-Alk-CONR}(\text{CH}_2\text{-CH}_2)_x\text{NR-}(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, $-\text{OOC-Alk-COO}(\text{CH}_2\text{-CH}_2)_x\text{O-}(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, $-\text{OOC-Alk-COO(AOX)}_x\text{-}(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, $-\text{OOC-Alk-CONR(AOX)}_x\text{-Alk-NR-}(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, or $-\text{O-}(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, wherein R, which can be the same or different, is hydrogen or a substituted or unsubstituted aryl or alkyl group, AOX represents an alkylene oxide group of from about 1 to about 12 carbons, and x is an integer between 1 and 500.

38. The modified pigment product of claim 19, wherein PP represents a polymer having the formula $[\text{A-(CR}_2\text{B)}_n\text{-CR}_2\text{A}]$, wherein A and B comprise a phenyl ether group and a substituted propanediyl group, R, which can be the same or different, is hydrogen or a substituted or unsubstituted aryl or alkyl group and n is an integer from 1 to 20.

39. The modified pigment product of claim 38, wherein A and B further comprise the photopolymerizable group.

40. The modified pigment product of claim 38, wherein:

A is $\begin{array}{c} \text{C}_6\text{H}_4- \\ | \\ \text{O-Y-T} \end{array}$ or $\begin{array}{c} \text{C}_6\text{H}_3(\text{CH}_3)- \\ | \\ \text{O-Y-T} \end{array}$ and

B is $\begin{array}{c} -\text{C}_6\text{H}_3- \\ | \\ \text{O-Y-T} \end{array}$ or $\begin{array}{c} -\text{C}_6\text{H}_2(\text{CH}_3)- \\ | \\ \text{O-Y-T} \end{array}$; wherein

Y is $-\text{CH}_2\text{-CH}(\text{Z})\text{-CH}_2-$, wherein Z is $-\text{OH}$, $-\text{OOC-Alk-COOH}$ or salt thereof, or a bond to Sp, and Alk represents a saturated or unsaturated cyclic or linear alkyl group; and

T is $\text{CH}_2=\text{CH-COO-}$ or $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COO-}$.

41. The modified pigment product of claim 40, wherein T comprises an alkyl ester.

42. The modified pigment product of claim 40, wherein Sp is $-\text{OOC-Alk-COO}-$, $-\text{OOC-Alk-CONR}-$, $-\text{OOC-Alk-CONR}(\text{CH}_2\text{-CH}_2)_x\text{NR}-(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, $-\text{OOC-Alk-COO}(\text{CH}_2\text{-CH}_2)_x\text{O}-(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, $-\text{OOC-Alk-COO(AOX)}_x-(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, $-\text{OOC-Alk-CONR(AOX)}_x\text{-Alk-NR}-(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, or $-\text{O}-(\text{CH}_2\text{-CH}_2)\text{-SO}_2-$, wherein R, which can be the same or different, is hydrogen or a substituted or unsubstituted aryl or alkyl group, AOX represents an alkylene oxide group of from about 1 to about 12 carbons, and x is an integer between 1 and 500.

43. The modified pigment product of claim 19, wherein the modified pigment product is in a liquid vehicle to form a dispersion.

44. The modified pigment product of claim 43, wherein the liquid vehicle is a non-aqueous vehicle comprising a solvent selected from the group consisting of: ethylcellosolve, ethylcellosolve acetate, butylcellosolve, butylcellosolve acetate, ethylcarbitol, ethylcarbitol acetate, diethyleneglycol, cyclohexanone, propyleneglycol monomethylether, propyleneglycol monomethylether acetate, lactate esters, and mixtures thereof.

45. The modified pigment product of claim 43, further comprising a photosensitive resin.

46. The modified pigment product of claim 45, wherein the photosensitive resin is a resin prepared from an epoxy bisphenol-A resin or an epoxy novolac resin.

47. A modified pigment product comprising a pigment having attached at least one polymeric group, wherein the pigment is carbon black having a dibutylphthalate absorption (DBP) of from about 25 to 70 mL/100g.

48. The modified pigment product of claim 47, wherein the modified pigment product is in a liquid vehicle to form a dispersion.

49. The modified pigment product of claim 48, wherein the liquid vehicle is a non-aqueous vehicle comprising a solvent selected from the group consisting of ethylcellosolve, ethylcellosolve acetate, butylcellosolve, butylcellosolve acetate, ethylcarbitol, ethylcarbitol acetate, diethyleneglycol, cyclohexanone, propyleneglycol monomethylether, propyleneglycol monomethylether acetate, lactate esters, and mixtures thereof.

50. The modified pigment product of claim 48, further comprising a photosensitive resin.

51. The modified pigment product of claim 50, wherein the photosensitive resin is a resin prepared from an epoxy bisphenol-A resin or an epoxy novolac resin.

52. A black matrix formed by applying a photosensitive layer onto a substrate, irradiating the photosensitive layer imagewise, and developing and drying the coating, wherein the photosensitive layer comprises a modified black pigment product comprising a black pigment having attached at least one polymeric group, wherein the polymeric group comprises at least one photopolymerizable group and at least one ionic or ionizable group.

53. The black matrix of claim 52 further comprising a photosensitive resin.

54. The black matrix of claim 52, wherein the black matrix has a volume resistivity of greater than or equal to 10^{13} ohm-cm.

55. The black matrix of claim 54, wherein the black matrix has an optical density of about 3 at a thickness of about 1 micron.

56. The black matrix of claim 52, wherein the black pigment is a carbon product.

57. The black matrix of claim 56, wherein the carbon product is a carbon black having a dibutylphthalate absorption of from about 25 to 70 mL/100g.
58. The black matrix of claim 52, wherein the polymeric group comprises a phenyl ether group and a substituted propanediyl group.
59. The black matrix of claim 52, wherein the polymeric group comprises a polymer prepared from epoxy bisphenol-A, oligomers of epoxy bisphenol-A, or epoxy novolac.
60. A black matrix formed by applying a photosensitive layer onto a substrate, irradiating the photosensitive layer imagewise, and developing and drying the coating, wherein the photosensitive layer comprises a modified black pigment product comprising a black pigment having attached at least one polymeric group having the formula $-X-Sp-[PP]$, wherein X, which is directly attached to the pigment, represents an arylene, a heteroarylene, or an alkylene group, Sp represents a spacer group, and PP represents a polymer optionally comprising at least one photopolymerizable group, at least one ionic or ionizable group, or both.
61. The black matrix of claim 60, further comprising a photosensitive resin.
62. The black matrix of claim 60, wherein the black matrix has a volume resistivity of greater than or equal to 10^{13} ohm-cm.
63. The black matrix of claim 62, wherein the black matrix has an optical density of about 3 at a thickness of about 1 micron.
64. The black matrix of claim 60, wherein the black pigment is a carbon product.
65. The black matrix of claim 64, wherein the carbon product is a carbon black having a dibutylphthalate absorption of from about 25 to 70 mL/100g.

66. The black matrix of claim 60, wherein the polymeric group comprises a phenyl ether group and a substituted propanediyl group.

67. The black matrix of claim 60, wherein PP comprises a polymer prepared from epoxy bisphenol-A, oligomers of epoxy bisphenol-A, or epoxy novolac.

68. The black matrix of claim 60, wherein PP represents a polymer having the formula [T-Y-(Q-Y)_n-T], wherein Q comprises a bisphenyl ether group, Y comprises a substituted propanediyl group, T comprises a terminating group, and n is an integer from 1 to 20.

69. The black matrix of claim 68, wherein T comprises the photopolymerizable group.

70. The black matrix of claim 68, wherein T comprises an alkyl ester.

71. The black matrix of claim 68, wherein:

Q is $-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-$, $-\text{O}-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{O}-$, or $-\text{O}-\text{C}_6\text{H}_4-$ fluorenyl- $\text{C}_6\text{H}_4-\text{O}-$;

Y is $-\text{CH}_2-\text{CH}(\text{Z})-\text{CH}_2-$, wherein Z is $-\text{OH}$, $-\text{OOC-Alk-COOH}$, or salt thereof, or a bond to Sp, and Alk represents a saturated or unsaturated cyclic or linear alkyl group; and

T is $\text{CH}_2=\text{CH}-\text{COO}-$ or $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-$.

72. The black matrix of claim 71, wherein Sp is $-\text{OOC-Alk-COO}-$, $-\text{OOC-Alk-CONR}-$, $-\text{OOC-Alk-CONR}(\text{CH}_2-\text{CH}_2)_x\text{NR}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, $-\text{OOC-Alk-COO}(\text{CH}_2-\text{CH}_2)_x\text{O}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, $-\text{OOC-Alk-COO(AOX)}_x(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, $-\text{OOC-Alk-CONR(AOX)}_x\text{Alk-NR}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, or $-\text{O}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, wherein R, which can be the same or different, is hydrogen or a substituted or unsubstituted aryl or alkyl group, AOX represents an alkylene oxide group of from about 1 to about 12 carbons, and x is an integer between 1 and 500.

73. The black matrix of claim 60, wherein PP represents a polymer having the formula [A-(CR₂B)_n-CR₂A], wherein A and B comprise a phenyl ether group and a substituted propanediyl group, R, which can be the same or different, is hydrogen or a substituted or unsubstituted aryl or alkyl group and n is an integer from 1 to 20.

74. The black matrix of claim 73, wherein A and B further comprise the photopolymerizable group.

75. The black matrix of claim 73, wherein:

A is $\begin{array}{c} \text{C}_6\text{H}_4- \\ | \\ \text{O}-\text{Y}-\text{T} \end{array}$ or $\begin{array}{c} \text{C}_6\text{H}_3(\text{CH}_3)- \\ | \\ \text{O}-\text{Y}-\text{T} \end{array}$ and

B is $\begin{array}{c} -\text{C}_6\text{H}_3- \\ | \\ \text{O}-\text{Y}-\text{T} \end{array}$ or $\begin{array}{c} -\text{C}_6\text{H}_2(\text{CH}_3)- \\ | \\ \text{O}-\text{Y}-\text{T} \end{array}$; wherein

Y is $-\text{CH}_2-\text{CH}(\text{Z})-\text{CH}_2-$, wherein Z is $-\text{OH}$, $-\text{OOC-Alk-COOH}$ or salt thereof, or a bond to Sp, and Alk represents a saturated or unsaturated cyclic or linear alkyl group; and

T is $\text{CH}_2=\text{CH-COO-}$ or $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO-}$.

76. The black matrix of claim 75, wherein T comprises an alkyl ester.

77. The black matrix of claim 75, wherein Sp is $-\text{OOC-Alk-COO-}$, $-\text{OOC-Alk-CONR-}$, $-\text{OOC-Alk-CONR}(\text{CH}_2-\text{CH}_2)_x\text{NR}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, $-\text{OOC-Alk-COO}(\text{CH}_2-\text{CH}_2)_x\text{O}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, $-\text{OOC-Alk-COO(AOX)}_x-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, $-\text{OOC-Alk-CONR(AOX)}_x\text{-Alk-NR}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, or $-\text{O}-(\text{CH}_2-\text{CH}_2)-\text{SO}_2-$, wherein R, which can be the same or different, is hydrogen or a substituted or unsubstituted aryl or alkyl group, AOX represents an alkylene oxide group of from about 1 to about 12 carbons, and x is an integer between 1 and 500.

78. A black matrix formed by applying a photosensitive layer onto a substrate, irradiating the photosensitive layer imagewise, and developing and drying the coating, wherein the photosensitive layer comprises a modified black pigment product

comprising a black pigment having attached at least one polymeric group, wherein the black pigment is carbon black having a dibutylphthalate absorption (DBP) of from about 25 to 70 mL/100g.

79. The black matrix of claim 78, further comprising a photosensitive resin.

80. The black matrix of claim 78, wherein the black matrix has a volume resistivity of greater than or equal to 10^{13} ohm-cm.

81. The black matrix of claim 80, wherein the black matrix has an optical density of about 3 at a thickness of about 1 micron.

82. A resin composition comprising: a) a photosensitive resin and b) a modified pigment product comprising a pigment having attached at least one polymeric group, wherein the polymeric group comprises at least one photopolymerizable group and at least one ionic or ionizable group, wherein the resin composition has been cured by irradiation.

83. A resin composition comprising: a) a photosensitive resin and b) a modified pigment product comprising a pigment having attached at least one polymeric group having the formula $-X-Sp-[PP]$, wherein X, which is directly attached to the pigment, represents an arylene, a heteroarylene, or an alkylene group, Sp represents a spacer group, and PP represents a polymer comprising at least one photopolymerizable group and at least one ionic or ionizable group, wherein the resin composition has been cured by irradiation.

84. A resin composition comprising: a) a photosensitive resin and b) a modified pigment product comprising a pigment having attached at least one polymeric group, wherein the pigment is carbon black having a dibutylphthalate adsorption (DBP) of from about 25 to 70 mL/100g.

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(54) Title: MODIFIED PIGMENT PRODUCTS AND BLACK MATRIXES COMPRISING SAME

(57) Abstract: The present invention describes modified pigment products comprising a pigment having attached at least one photopolymerizable group and at least one ionic or ionizable group. Dispersions, black matrixes, and resin compositions comprising these modified pigment products are also disclosed.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/00277A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09C1/56 C09C3/10 C08K9/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09C C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 31175 A (CABOT CORP) 24 June 1999 (1999-06-24)	1,52,82
Y	page 1, line 22 -page 3, line 5 page 5, line 13 -page 8, line 6 page 12, line 14 -page 13, line 24 claims; example 2	19,60,83
X	WO 00 22051 A (CABOT CORP) 20 April 2000 (2000-04-20) cited in the application page 4, line 4 - line 13 page 8, line 10 -page 10, line 10 page 12, line 20 -page 16, line 8 page 26, line 12 -page 27, line 2	1,52,82
	—	—/—

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 03/00277

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 475 075 A (XEROX CORP) 18 March 1992 (1992-03-18) page 2, line 3 - line 6 page 4, line 42 -page 7, line 51 claims; example 1 ----	1,52,82
P, Y	WO 02 04564 A (CABOT CORP) 17 January 2002 (2002-01-17) the whole document ----	19,60,83
A	US 5 837 045 A (BELMONT JAMES A ET AL) 17 November 1998 (1998-11-17) column 1, line 54 - line 61 column 3, line 9 - line 45 column 5, line 43 - line 48 example 1 ----	1
X	EP 0 987 303 A (NIPPON CATALYTIC CHEM IND) 22 March 2000 (2000-03-22) paragraphs '0012!, '0019!, '0029!, '0081!, '0099!, '0111!, '0134! ----	47-49,78
X	WO 00 68321 A (CABOT CORP) 16 November 2000 (2000-11-16) page 4, line 3 - line 11 page 8, line 1 - line 10 page 5, line 30 - line 33 page 13, line 9 - line 20 page 14, line 23 - line 25 page 15, line 18 -page 16, line 3 ----	47
X	PATENT ABSTRACTS OF JAPAN vol. 012, no. 223 (C-507), 24 June 1988 (1988-06-24) & JP 63 017917 A (NIPPON STEEL CHEM CO LTD), 25 January 1988 (1988-01-25) abstract ----	47
P, X	US 2002/189498 A1 (MCALWAIN THOMAS E ET AL) 19 December 2002 (2002-12-19) paragraphs '0013!, '0017!, '0021!, '0022!, '0031!-'0035! ----	47

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/00277

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-46, 52-77, 82-83

a modified pigment product, having attached a polymeric group comprising a photopolymerizable group and an ionic or ionizable group

2. Claims: 47-51, 78-81, 84

a modified pigment product, having attached a polymeric group wherein the pigment is carbon black having a DBP absorption of 25 to 70 ml/100g

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/00277

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
WO 9931175	A 24-06-1999	US	6110994 A	29-08-2000
		AU	1724299 A	05-07-1999
		BR	9813577 A	13-02-2002
		CA	2314226 A1	24-06-1999
		EP	1040160 A1	04-10-2000
		JP	2002508422 T	19-03-2002
		WO	9931175 A1	24-06-1999
		ZA	9811536 A	15-06-2000
WO 0022051	A 20-04-2000	US	6458458 B1	01-10-2002
		AU	6421299 A	01-05-2000
		CA	2347093 A1	20-04-2000
		EP	1124905 A1	22-08-2001
		JP	2002527564 T	27-08-2002
		WO	0022051 A1	20-04-2000
EP 0475075	A 18-03-1992	US	5281261 A	25-01-1994
		CA	2046571 A1	01-03-1992
		DE	69114962 D1	11-01-1996
		DE	69114962 T2	18-04-1996
		EP	0475075 A1	18-03-1992
		JP	3048692 B2	05-06-2000
		JP	4234467 A	24-08-1992
WO 0204564	A 17-01-2002	AU	7308501 A	21-01-2002
		EP	1307513 A2	07-05-2003
		WO	0204564 A2	17-01-2002
		US	2002011185 A1	31-01-2002
US 5837045	A 17-11-1998	AU	3232897 A	07-01-1998
		DE	69711040 D1	18-04-2002
		DE	69711040 T2	19-09-2002
		EP	0906371 A1	07-04-1999
		JP	2000513396 T	10-10-2000
		TW	426716 B	21-03-2001
		WO	9748769 A1	24-12-1997
EP 0987303	A 22-03-2000	JP	2000154327 A	06-06-2000
		EP	0987303 A1	22-03-2000
		US	6417283 B1	09-07-2002
WO 0068321	A 16-11-2000	AU	4987700 A	21-11-2000
		EP	1185590 A1	13-03-2002
		WO	0068321 A1	16-11-2000
		US	6372820 B1	16-04-2002
JP 63017917	A 25-01-1988		NONE	
US 2002189498	A1 19-12-2002	WO	02088258 A1	07-11-2002